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14. ABSTRACT The PI has demonstrated for the first time that hyperthermal energy atomic oxygen ions can directly abstract oxygen atoms from and deposit oxygen atoms into a silicon oxide surface. Isotopic labeling and 2-D velocity-resolved detection have allowed for the unambiguous assignment of two distinct abstraction mechanisms. In the first, an incident oxygen ion scatters from the lattice and abstracts an oxygen atom on the ion's departure from the surface. In the second mechanism, the energetic atomic oxygen ion generates an oxygen recoil, that in turn abstracts a neighboring oxygen atom from the silicon oxide lattice. In concert with the etching of oxygen from the surface, many of the incident oxygen ions become incorporated into the silicon oxide lattice. Isotopic labeling experiments have measured the cross section by which hyperthermal oxygen projectiles are incorporated into the topmost layer of the silicon oxide film. The largest rates of incorporation occur for 5 eV oxygen ions. These state-of-the-art experiments have demonstrated that the bombardment of silicon oxide with hyperthermal oxygen ions, such as in a LEO environment, can lead to changes in the gas/solid interface.					
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Ion/Surface Interactions and Reaction Mechanisms

by
Dennis C. Jacobs

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1. Executive Summary

The primary goal of this research grant was to characterize many of the fundamental reaction mechanisms operative when hyperthermal energy ions collide with well-characterized surfaces. Specifically, the reaction of O^+ with silicon oxide was explored across the hyperthermal energy range. The incident ions were responsible for both growing and etching the oxide film under steady-state conditions. This project characterized the relevant reaction mechanisms under conditions where the surface was being actively modified by the incident ion beam. The results of this study enhance our understanding of the ways in which spacecraft materials can degrade in low-earth orbit (LEO). Furthermore, ion beam oxidation is important to the semiconductor processing industry as a promising technique for growing thin oxide films on silicon under room temperature conditions.

Isotopic labeling experiments, combined with mass-, energy-, and angular-resolved detection, revealed a competition between abstraction and sputtering mechanisms in the emergence of O_2^- and SiO^+ products. At collision energies above 16 eV, an incident O^+ ion can neutralize on approach to the surface, scatter from the lattice, and pick up an oxygen atom on the outbound trajectory (scattering mediated abstraction). The resulting O_2^- ion scatters in the forward direction with approximately 15% of the initial O^+ kinetic energy. At collision energies above 33 eV, a second reaction channel for O_2^- emergence opens up. Here, the incident projectile creates an O-atom recoil upon impact. As the oxygen recoil leaves the surface, it abstracts a neighboring oxygen atom from the lattice to form scattered O_2^- (recoil abstraction). Notwithstanding, the same O^+ beam is also responsible for further oxidizing silicon in the 30 Å oxide layer.

The incorporation of incident O^+ ions into a silicon oxide layer was also studied quantitatively using isotopic labeling experiments. The largest rate of oxygen incorporation into the topmost layer of silicon oxide occurred when the incident O^+ ions

approached with 5 eV kinetic energy. At larger collision energies, it is believed that the oxygen ion implants and is incorporated deeper into the oxide film. This was the first direct measurement of the cross section for ion incorporation into silicon oxide at hyperthermal energies.

Through this AFOSR grant, a graduate student (Xiangdong Qin) and a postdoc (Tochko Tzvetkov) have received invaluable scientific training. The research has been presented at the following conferences:

- Contributed talk at the American Physical Society National Meeting, Seattle, WA, April, 2001
- Invited talk at the National Meeting of the American Chemical Society, San Diego, CA, April, 2001
- Poster at the Molecular Dynamics AFOSR Contractor's Meeting, Irvine, CA, May, 2001
- Invited talk at the 19th International Conference on Atomic Collisions in Solids, Paris, France, July, 2001
- Contributed poster at the Gordon Conference on Dynamics at Surfaces, Andover, NH, August, 2001

The research findings have been reported in the following publications:

- Quinteros, C. L., Tzvetkov, T., Qin, X., and Jacobs, D. C. (2001) "Reactive Scattering of O⁺ on oxidized Si(001) " *Nuclear Instruments and Methods in Physics Research B*, **182**, 187 – 192.
- Maazouz, M., Quinteros, C. L., Tzvetkov, T., Maazouz, P. L., Qin, X., Barstis, T. L. O. and Jacobs, D. C. (2001) "Reactive Collisions of Hyperthermal Ions with Oxide

Surfaces " in *Applications of Accelerators in Research and Industry*, edited by J.L. Duggan and I. L. Morgan, American Institute of Physics, **576**, 122-125.

- Quinteros, C. L., "Reaction Dynamics and Energy Transfer in Ion/Surface Scattering: O^+/SiO_2 and $Ne^+/Si(001)$ ", Dissertation for the Ph.D., University of Notre Dame (2001).
- Jacobs, D. C. (2002) "Reactive Collisions of Hyperthermal Energy Molecular Ions with Solid Surfaces" in *Annual Review of Physical Chemistry*, **53**, 379-407.

2. Introduction

An orbiting space vehicle is continuously exposed to a flux of energetic neutral atoms/molecules, ions, electrons, charged particle radiation, electromagnetic radiation, meteoroids, and orbital debris. This hostile environment can adversely impact the longevity and success of a spacecraft's mission through material degradation, radiation damage, electrostatic charging/arcing, aerodynamic drag, etc.¹ To better understand the dynamics of ion/surface collisions, the processes of energy transfer, charge transfer, atom abstraction, and deposition were explored under well-defined scattering conditions. Detailed mechanisms are presented that can be incorporated into existing models of space vehicle interactions with the low-earth or transfer orbit environments.

The experimental approach is to direct monoenergetic, mass-selected ions at well-characterized surfaces under ultrahigh vacuum conditions. The ensuing products are detected with mass-, charge-, energy- and angular-resolution. The reaction dynamics are extracted by observing how the product distributions depend on the initial conditions.²

3. Experimental Approach

An ultrahigh vacuum scattering chamber has been constructed to explore the fundamental processes that occur when hyperthermal energy ions impact surfaces under highly controlled conditions.³ The apparatus depicted in Fig. 1 consists of four differentially pumped chambers: the source and buffer chambers contain the ion transport optics; the main scattering chamber houses the surface sample and diagnostic tools; and the rotatable detector chamber contains a quadrupole mass spectrometer (QMS). The main chamber is pumped by both a cryopump and an ion pump.

Ions extracted from a Colutron discharge source are accelerated to 1.5 keV, pass through a gas cell for filtering out metastable states, are mass-selected within a Wein

filter, and decelerate to the final beam energy (5 –300 eV). This design delivers up to 20 nA of O^+ ion current to the surface in a target area of approximately 1 mm².

The surface sample is heated resistively or by electron bombardment, and the sample mount is cooled by a liquid nitrogen reservoir. A load lock chamber allows surface samples to be introduced to the main chamber and secured to the manipulator without venting the system. The main scattering chamber is further divided into two sections. The top tier is equipped with routine surface science preparation and analysis tools: low energy electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), Residual Gas Analyzer (RGA), Kelvin probe for work function measurements, capillary array gas doser, an alkali-atom source, and an ion gun for sputtering the surface clean.

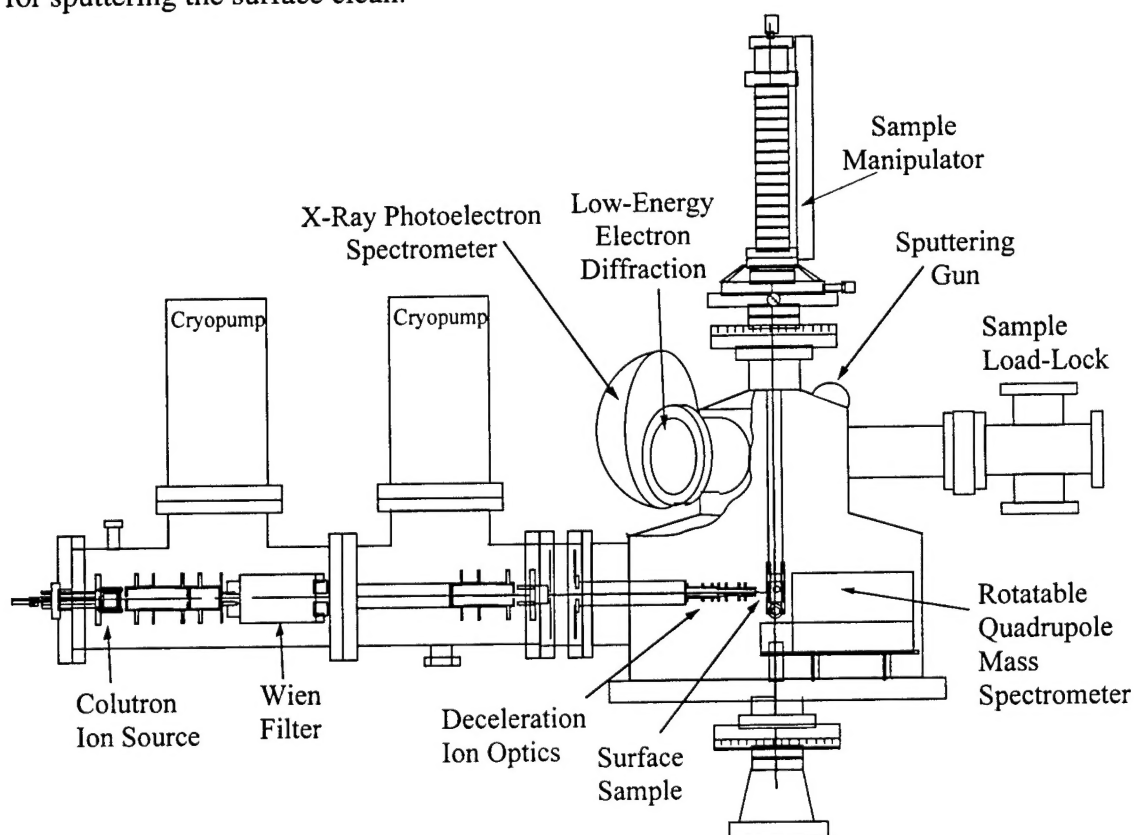


Figure 1. Atomic Ion/Surface Scattering Apparatus

Scattering experiments take place in the lower tier of the main chamber. Here a sensitive QMS detector counts individual scattered particles with angle-, energy-, and mass-resolution. Both positive and negative ions are collected with high efficiency. Furthermore, XPS, Kelvin probe measurements, and temperature-programmed desorption (TPD) are utilized to characterize the surface composition before and after ion beam exposure. In this way, surface modifications induced by energetic particle bombardment are detected.

Two computer data acquisition systems control all the ion optics' potentials and monitor the spectrometer signals. At a series of collision energies, the scattered energy distribution for each product channel is recorded. The angle of incidence and the detection angle are independently varied.

4. Reaction of Hyperthermal O^+ with Silicon Oxide Thin Films

Ion beam oxidation is an effective way to grow thin oxide films on silicon at room temperature. A continuous beam of atomic oxygen ions efficiently oxidizes clean Si(100), producing a 30 Å-thick oxide film.⁴ Although the oxide layer does not appear to grow thicker, the interaction of atomic oxygen ions with the silicon oxide layer forms a dynamic interface. Energetic oxygen ions will etch the interface, generating gaseous molecular oxygen and SiO products. A fraction of the incident oxygen ions will also be incorporated into the silicon oxide film. As an additional effect, the energetic bombardment of ions helps to transport oxygen atoms deeper into the film. The collective result of prolonged O^+ exposure is a 30 Å SiO_x layer that recedes deeper into the Si crystal with time. The reaction channels operative in this system are analogous to those that may occur on the surfaces of spacecraft in low-earth orbit.⁵ Silicon oxide is a

transparent film commonly employed as a protective layer on the external surfaces of spacecraft. It is important to understand how silicon oxide responds to the continuous bombardment of energetic oxygen atoms and ions.

The scattering of O^+ on SiO_x has been conducted at collision energies varying from 5 eV to 150 eV.⁶ Although the incident particles are oxygen ions, efficient neutralization along the inbound trajectory delivers virtually 100% O-atoms to the surface. It is unclear as to whether the nascent electron-hole formed in the SiO_x surface delocalizes faster than the time scale of the collision. If the hole resulting from neutralization exerts no influence on the ensuing collision dynamics, then the following experiments apply equally well to understanding the interaction of hyperthermal O-atoms with silicon oxide.

Incident O^+ ions are observed to abstract an oxygen atom from the SiO_x lattice and scatter into the vacuum as O_2^- .³ Isotopic labeling experiments have established that two reaction mechanisms are responsible for the emergence of O_2^- . At collision energies above 16 eV, an incident O^+ ion can neutralize on approach to the surface, scatter from the lattice, and pick up an oxygen atom on the outbound trajectory (scattering mediated abstraction). The resulting O_2^- ion scatters in the forward direction with approximately 15% of the initial O^+ kinetic energy. At collision energies above 33 eV, a second reaction channel for O_2^- emergence opens up. Here, the incident projectile creates an O-atom recoil upon impact. As the oxygen recoil leaves the surface, it abstracts a neighboring oxygen atom from the lattice to form scattered O_2^- (recoil abstraction). Figure 2 compares the relative yields of O_2^- resulting from the two abstraction mechanisms.⁷ These two reaction pathways demonstrate some of the ways in which a hyperthermal O^+ beam will etch away a silicon oxide layer. Notwithstanding, the same O^+ beam is also responsible for further oxidizing silicon in the 30 Å oxide layer.

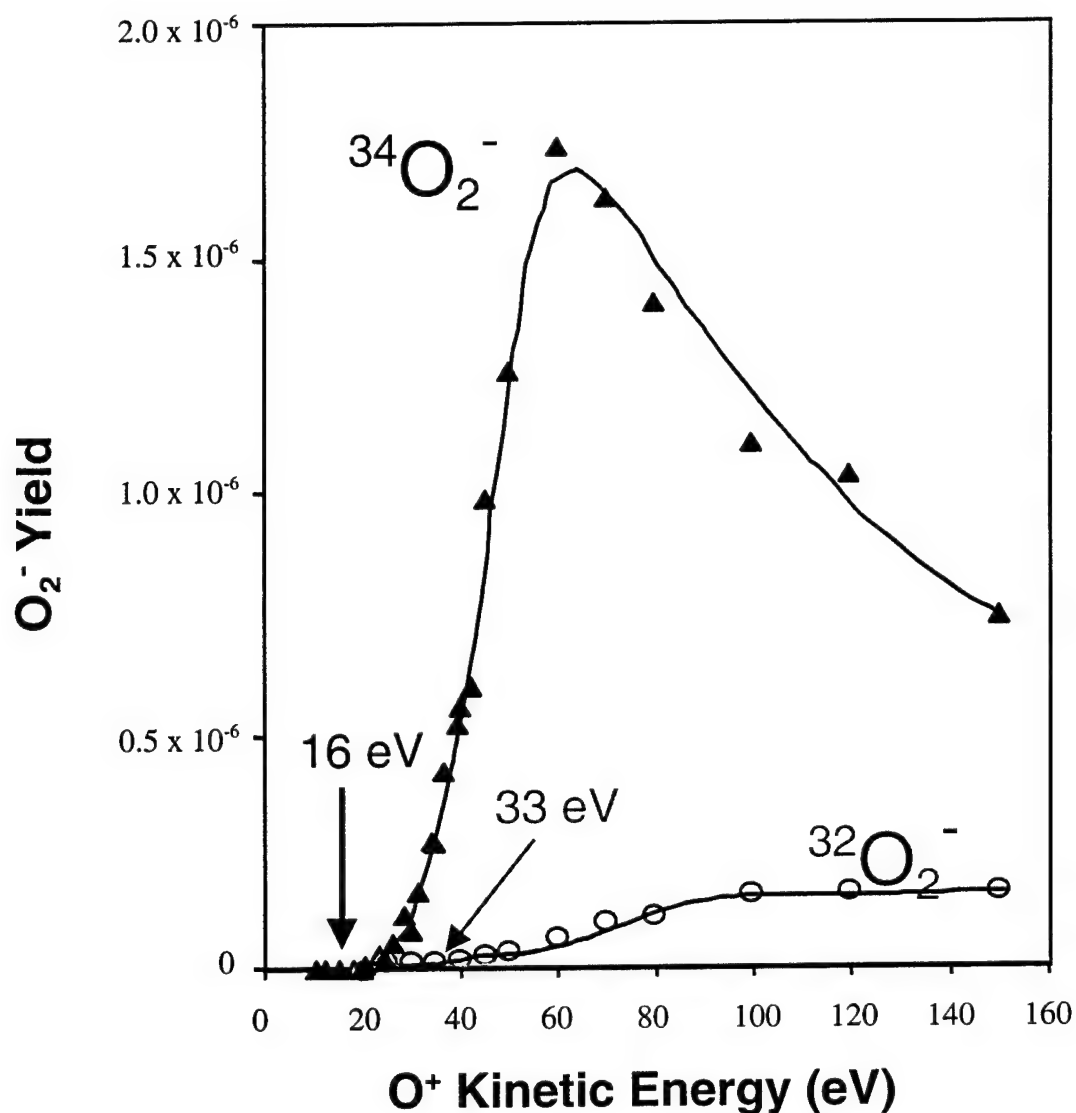


Figure 2. Relative yields of O_2^- versus incident O^+ energy. The mechanisms for O_2^- emergence are assigned to scattering mediated abstraction ($^{34}O_2^-$) and recoil abstraction ($^{32}O_2^-$).

Figure 3 shows the scattered O^- intensity during the first stages of the O^+ dose. The sudden rise in the O^- yield corresponds to the growth phase of the film. In the plateau region, the chemical composition of the topmost layer of the film remains in a steady state, where the rate of further oxidation is matched by the rate of oxygen removal. Although it appears that the film is not changing in the plateau region, there is an appreciable uptake of incident oxygen ions.

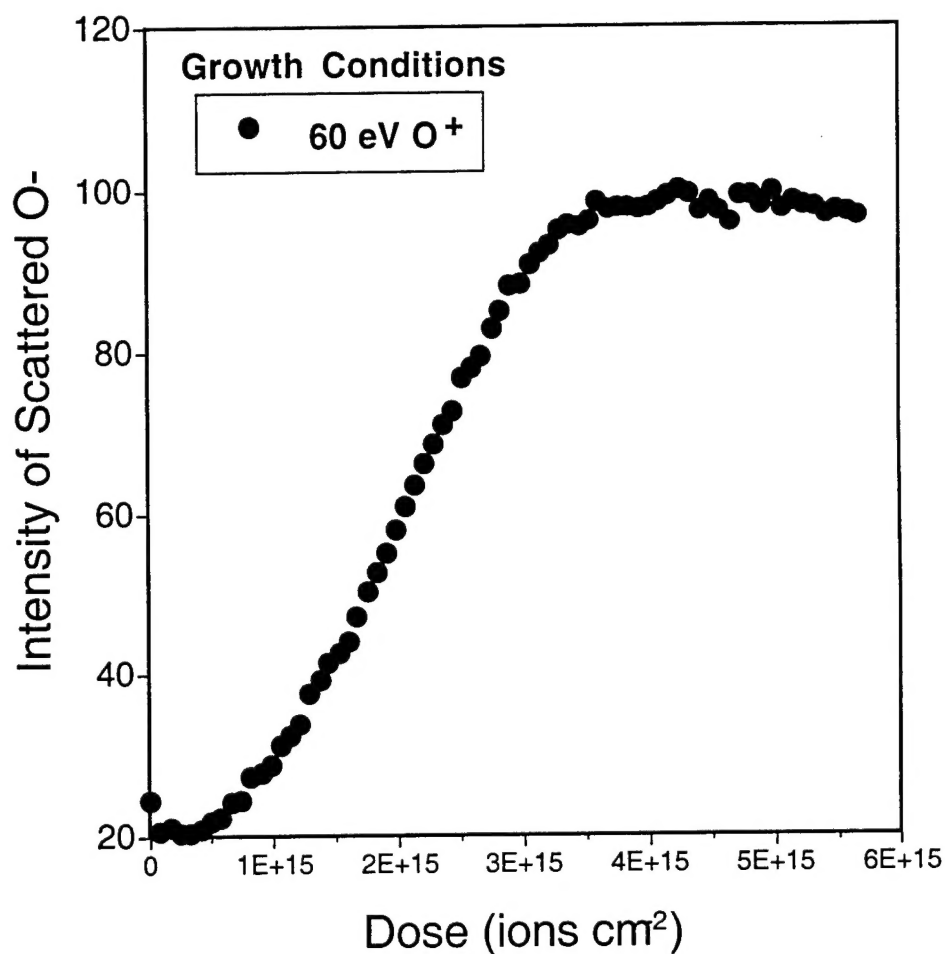


Figure 3. The intensity of scattered O⁻ as a function of the dose of O⁺ incident at 60 eV.

To measure the rate in which incident ions are incorporated into the film, an oxide layer is first grown with ¹⁶O⁺ until the saturation region is reached. Then, a beam of ¹⁸O⁺ is targeted at the surface, and the uptake of ¹⁸O into the Si¹⁶O_x film is monitored through the evolution of the isotopic composition of the film (See Fig. 4). The data can be fit by a single-parameter model. The fitting parameter corresponds to a cross section for incorporation, i.e., the area near an oxide site in which an incident ion must strike in order to replace the current oxygen atom at the site. This model does not distinguish where the former oxygen atom goes. It could be sputtered into the vacuum or it could diffuse down deeper into the film. Figure 5 shows how the cross section for incorporation varies with

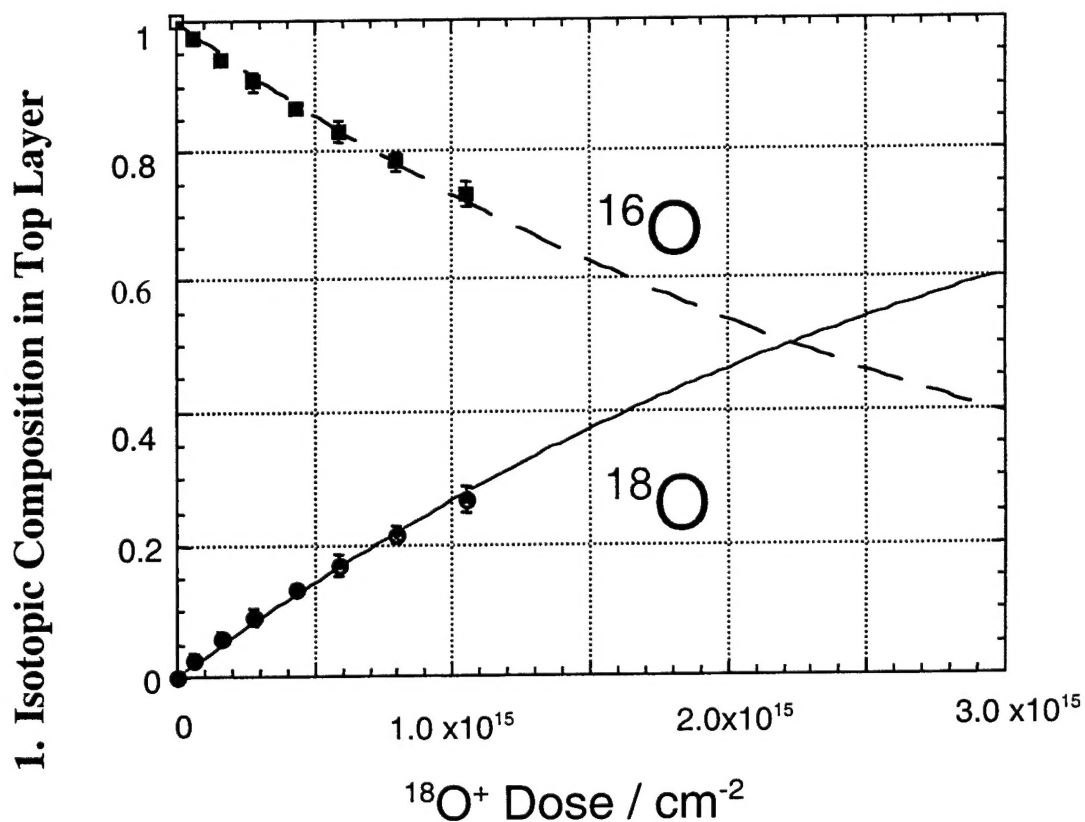


Figure 4. Isotopic composition of oxygen in the topmost layer following $^{18}\text{O}^+$ dose on Si^{16}O thin film.

the O^+ beam energy.⁸ As the beam energy increases, the cross section for incorporating oxygen into the topmost layer decreases. Presumably, this is because the more energetic oxygen ions implant deeper into the lattice. The isotopic ratio measured in these experiments corresponds only to the oxygen atoms found in the topmost layer of silicon oxide thin film.

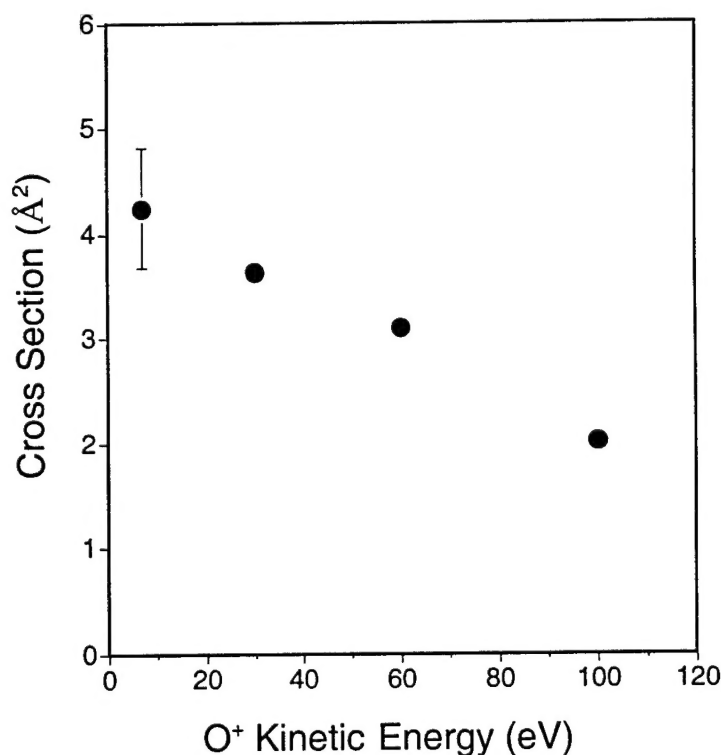


Figure 5. Cross section for incorporation of incident O^+ into the topmost layer of a SiO_x thin film versus the energy of the incident ion beam.

5. Conclusions

Ion beam oxidation of Si(001) by 5 – 150 eV O^+ ions produces a thin SiO_2 film, approximately 30 Å thick. Further O^+ bombardment does not increase the thickness of the film; rather, the O^+ ions oxidize the surface at a rate equal to the rate at which Si and O are removed from the surface through abstraction and sputtering mechanisms.³ Cross sections for incorporating incident O-atoms into the film indicate that there is facile exchange at the interface. Taken together these experiments provide the most detailed view of ion beam oxidation of silicon. They also establish some of the degradation pathways by which SiO_x protective layers may be compromised in LEO environments.

6. References

- ¹ D. C. Jacobs, "Dynamics of Hypervelocity Gas/Surface Collisions," in *Chemical Dynamics in Extreme Environments*, edited by R. Dressler, *Advanced Series in Physical Chemistry*, World Scientific Publishers, 349 (2000).
- ² D. C. Jacobs, *Annual Review of Physical Chemistry*, **53**, 379-407 (2002).
- ³ C. L. Quinteros, T. Tzvetkov, and D. C. Jacobs, *Journal of Chemical Physics*, **113**, 5119-5122(2000).
- ⁴ S. E. Todorov and E. R. Fossum, *J. Vac. Sci. Technol. B* **6**, 466 (1988).
- ⁵ E. Murad, *Annu. Rev. Phys. Chem.* **49**, 73 (1998).
- ⁶ Maazouz, M., Quinteros, C. L., Tzvetkov, T., Maazouz, P. L., Qin, X., Barstis, T. L. O. and Jacobs, D. C. in *Applications of Accelerators in Research and Industry*, edited by J.L. Duggan and I. L. Morgan, American Institute of Physics, **576**, 122-125 (2001).
- ⁷ C. L. Quinteros, T. Tzvetkov, X. Qin, and D. C. Jacobs, *Nucl. Instrum. Meth. B*, **182**, 187 (2001).
- ⁸ X. Qin, T. Tzvetkov, C. L. Quinteros, and D. C. Jacobs, *in preparation*.